

## The influence of sea water composition on the apparent constants of the carbonate system

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**Abstract**—The sea water model of GARRELS and THOMPSON (1962) has been applied to estimate variations in the apparent constants of the carbonate system in sea water. Analyses show that for open ocean water, corrections are negligible (less than 1%);, whereas in interstitial water of marine sediments  $K_2'$  and  $K'_{sp}$  variations may reach  $\pm 10\%$ . Experimental procedures used by some investigators to determine the solubility of  $\text{CaCO}_3$  in sea water, may have resulted in erroneous values, due to deviation of tested solutions from the average composition of sea water. Values for solubility product of  $\text{CaCO}_3$  in sea water of 19‰ Cl at 25°C given by MACINTYRE (1965), are too high by at least 6%, as determined by the present analysis.

### INTRODUCTION

THE CHEMISTRY of the  $\text{CO}_2$ – $\text{CaCO}_3$  system, in the ocean is conveniently described using relationships involving apparent dissociation constants (HARVEY, 1957; LYMAN, 1957; SKIRROW, 1965; PYTKOWICZ, 1969; PARK, 1969). First and second apparent dissociation constants of carbonic acid are defined as (LYMAN, 1957):

$$K_1'(T, P, \text{Cl } \%) = \frac{a\text{H} [\text{HCO}_3^-]_t}{[\text{H}_2\text{CO}_3]_t} \quad (1)$$

$$K_2'(T, P, \text{Cl } \%) = \frac{a\text{H} [\text{CO}_3^{2-}]_t}{[\text{HCO}_3^-]_t} \quad (2)$$

where:

$a\text{H}$  = activity of hydrogen ion on the National Bureau of Standards pH scale

$[\text{H}_2\text{CO}_3]_t$  = total concentration of  $\text{CO}_2 + \text{H}_2\text{CO}_3$  in solution

$[\text{HCO}_3^-]_t$  = total concentration of bicarbonate ion.

$[\text{CO}_3^{2-}]_t$  = total concentration of carbonate ion.

The apparent solubility product of  $\text{CaCO}_3$  is defined as (MACINTYRE, 1965):

$$K'_{sp}(T, P, \text{Cl } \%) = [\text{Ca}^{2+}]_t [\text{CO}_3^{2-}]_t, \quad (3)$$

where:

$[\text{Ca}^{2+}]_t$  = total concentration of dissolved calcium.

Definitions of the thermodynamic constants are analogous to the corresponding apparent constants (HARNED and OWEN, 1958), but differ from them by being independent of compositional variation in solution. They are, therefore, the most desirable parameters for studying carbonate equilibria in sea water. Unfortunately, application of the thermodynamic constants requires knowledge of all ion-pairing equilibria in sea water and activity coefficients of all ions over the temperature and pressure range

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of interest. Sufficient data are not yet available for the application of thermodynamic constants with the precision obtained by using measured apparent constants (EDMOND and GIESKES, 1970).

The apparent dissociation constants of the carbonate system in sea water are explicitly dependent upon solution composition, through the single variable chlorinity. This is possible because of the constancy of major ion ratios in sea water (CULKIN, 1965). Any variation in composition of solution which involves a departure in the chloride ion to major ion ratio, would be reflected in a change in  $K'$  from sea water values (LYMAN, 1957; GARRELS, THOMPSON and SIEVER, 1960; PYTKOWICZ, 1969). In this study, we have examined some examples where compositional effects might alter the values of apparent dissociation constants. The changes in the constants have been estimated using a modified version of the sea water model of GARRELS and THOMPSON (1962).

#### MODEL CALCULATIONS

The validity of the model of GARRELS and THOMPSON (1962) for ionic speciation in sea water has been checked by direct measurements using ion-selective electrodes (GARRELS and THOMPSON, 1962; THOMPSON and ROSS, 1966; GARRELS, 1967) and solubility studies (BERNER, 1965; PYTKOWICZ and GATES, 1968). An important feature of the model is that it can relate the commonly used apparent constants to the corresponding thermodynamic constants by:

$$K_1' = K_1 \frac{[\text{HCO}_3^-]_t [\text{H}_2\text{CO}_3]_f \gamma_{\text{H}_2\text{CO}_3}}{[\text{H}_2\text{CO}_3]_t [\text{HCO}_3^-]_f \gamma_{\text{HCO}_3^-}} \quad (4)$$

$$K_2' = K_2 \frac{[\text{CO}_3^{2-}]_t [\text{HCO}_3^-]_f \gamma_{\text{HCO}_3^-}}{[\text{HCO}_3^-]_t [\text{CO}_3^{2-}]_f \gamma_{\text{CO}_3^{2-}}} \quad (5)$$

$$K'_{\text{sp}} = K_{\text{sp}} \frac{[\text{Ca}^{2+}]_t [\text{CO}_3^{2-}]_t}{[\text{Ca}^{2+}]_f \gamma_{\text{Ca}^{2+}} [\text{CO}_3^{2-}]_f \gamma_{\text{CO}_3^{2-}}} \quad (6)$$

Assuming that the total concentrations (subscript  $t$ ), the single ion activity coefficients ( $\gamma$ ) and the dissociation constants ( $K$ ), are known, one can estimate the apparent constants ( $K'$ ) because the concentration of the free species (subscript  $f$ ) can be deduced from the model of Garrels and Thompson.

The calculation of  $K_1'$ ,  $K_2'$  using the sea water model of Garrels and Thompson has been performed previously (LAFON, 1969). The estimated value of  $K_1' = 0.97 \times 10^{-6}$  at 25°C agrees quite well with the measured value  $1.00 \times 10^{-6}$  (LYMAN, 1957). The agreement is not as good in the case of  $K_2'$ ; the measured value is approximately 55% smaller than the calculated one. This discrepancy may be due to incomplete or incorrect data in the sea water model, although it has been suggested (TAKAHASHI, WEISS, CULVERSON, EDMOND, HAMMOND, WONG, LI and BAINBRIDGE, 1970) that Lyman's value is 30% too low.

Despite the discrepancies between measured and calculated values, it was assumed in the analyses described below that the ion pairing model can predict small *relative* changes in apparent dissociation constants due to compositional variations.

The mathematical procedure adopted here for solving the set of non-linear equations of the sea water model is similar to the iteration method described by

GARRELS and THOMPSON (1962) and BERNER (1971). The calculations were carried out on a small digital computer (PDP-8/L) by a program written in FOCAL (DIGITAL EQUIPMENT COMPANY, 1968). Calculations began by assuming that all ionic species are free, hence obtaining a first approximation of the associated species. These values were then used to calculate a better estimate of the free species from which the next estimate of the complexed species was obtained. The calculation was repeated until new estimates differed from previous ones by no more than one micro-mole. Five to six iterations were usually required to achieve this precision. Once the distribution of free and complexed ions was obtained,  $K_1'$ ,  $K_2'$  and  $K'_{sp}$  were calculated by equations (4)–(6).

All calculations were carried out for a model sea water of 19‰ Cl at 25°C. The assumed sea water composition, activity coefficients and dissociation constants are from BERNER (1971). Test calculations show that the single ion activity coefficient of any one species involved has a broad minimum at the ionic strength of sea water. Therefore, the present calculations were carried out under the assumption of constant activity coefficients. Model calculations show that the results are insensitive to small changes in sea water composition or values of thermodynamic constants. The contribution of borate to the apparent dissociation constants was neglected.

A normalized measure for the dependence of  $K_1'$ ,  $K_2'$  and  $K'_{sp}$  on change in the composition of sea water can be obtained by calculating a sensitivity parameter  $S_{K'}^i$  defined as:

$$S_{K'}^i = \frac{\Delta K'/K'}{\Delta n_i/n_i} \quad (7)$$

where  $K'$  is an apparent constant ( $K_1'$ ,  $K_2'$  or  $K'_{sp}$ ) and  $n$  is the total concentration of an ion species,  $i$ .

The sensitivity parameters of the apparent constants with respect to the major ions in sea water are given in Table 1. All the sensitivity parameters are smaller than one,

Table 1. Sensitivity of  $K_1'$ ,  $K_2'$ ,  $K'_{sp}$  to a change in sea water composition.

$$S_{K'}^i = \frac{\Delta K'/K'}{\Delta n_i/n_i}$$

Ion (i)	$S_{K'}^i \times 10^3$		
	$K'_{sp}$	$K_1'$	$K_2'$
K <sup>+</sup>	−0.05	0.11	0.32
Na <sup>+</sup>	180.67	88.42	111.06
Mg <sup>2+</sup>	640.54	155.05	442.24
Ca <sup>2+</sup>	70.90	33.73	38.85
SO <sub>4</sub> <sup>2−</sup>	9.15	−18.93	−53.98
HCO <sub>3</sub> <sup>−</sup>	2.08	−0.97	−2.75
CO <sub>3</sub> <sup>2−</sup>	−0.34	−0.56	−0.17
Cl <sup>−</sup>	0	0	0

which implies that the percentage change in  $K_1'$ ,  $K_2'$  and  $K'_{sp}$  is always smaller than the percentage change in  $n$ . The apparent constants are most sensitive to changes in magnesium concentration and least sensitive to variation in potassium. This results from the fact that about 13% of magnesium is complexed whereas only about 1%

of potassium is associated with other ions (GARRELS and THOMPSON, 1962; BERNER, 1971). The sensitivity parameter to chloride is zero, as this ion does not form any ion pair according to the model of Garrels and Thompson. A first approximation of the total expected change of the apparent constants can be obtained from Table 1 by summing the individual changes in the constants due to the changes in ionic concentrations.

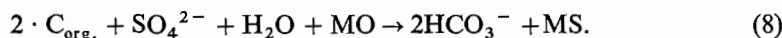
The anions' sensitivity of the apparent constants is generally smaller than that of cations, even though a large percentage of the anion species are complexed. This is due to the fact that the total concentration of anions, excluding  $\text{Cl}^-$ , is relatively small, and even a large percentage change in their concentration amounts to only a small absolute change in concentration.

Maximum relative change in concentration of cations in open ocean waters is probably 2% (CULKIN, 1965), which will result in only a 1% change in the apparent constants. However, the overall change in bicarbonate and carbonate concentration is larger, as they are pH-dependent (SKIRROW, 1965). The apparent constants are relatively insensitive to maximum bicarbonate or carbonate variation in open ocean waters, and for all practical purposes,  $K_1'$ ,  $K_2'$  and  $K'_{sp}$  in open ocean waters can be considered to be only a function of chlorinity and temperature. In fact, the expected changes in the constants due to compositional changes of open ocean waters are much smaller than the uncertainty in the values of these constants (EDMOND and GIESKES, 1970).

#### INTERSTITIAL WATERS OF MARINE SEDIMENTS

The composition of interstitial waters of recent marine sediments may differ from that of average sea water (SIEVER, BECK and BERNER, 1965; BERNER, 1965; PRESLEY and KAPLAN, 1968; PRESLEY, 1969), although the total salinity may not appreciably change. As the apparent constants  $K_1'$ ,  $K_2'$  and  $K'_{sp}$  were carefully measured as a function of chlorinity and temperature (LYMAN, 1957; MACINTYRE, 1965; EDMOND and GIESKES, 1970)—and as no experimental data is available for other compositions—one is inclined to apply these constants to interpret the carbonate system in interstitial waters (PRESLEY and KAPLAN, 1968). Such a procedure can only be justified if the variations of the apparent constants, due to the compositional changes, are smaller than the uncertainty limits set for the analysis. Of particular interest is the case of interstitial waters of anoxic marine sediments, which are characterized by sulfate depletion and marked alkalinity increase due to the activity of sulfate-reducing bacteria (ZOBELL and RITTENBERG, 1948).

Oxidation of organic carbon ( $C_{org.}$ ) by sulfate-reducing bacteria can be represented schematically by:



This model assumes that the sulfide is precipitated as metal sulfide (MS) and that the produced  $\text{CO}_2$  is in the form of bicarbonate at the pH of the interstitial waters. Metals are assumed to be originally present as metal oxides (MO). Under these conditions, the increase in carbonate alkalinity ( $\Delta\text{CA}$ ) is equal to twice the amount of sulfate reduced (RICHARDS, 1965).

$$\Delta\text{CA} = -2\Delta\text{SO}_4^{2-}. \quad (9)$$

Carbonate alkalinity is related to the carbonate species by (SKIRROW, 1965):

$$CA = [\text{HCO}_3^-]_r + 2[\text{CO}_3^{2-}]_r \quad (10)$$

and hence, (neglecting borate alkalinity):

$$[\text{HCO}_3^-]_r + 2[\text{CO}_3^{2-}]_r = \text{TA}_0 - 2\Delta\text{SO}_4^{2-} \quad (11)$$

where  $\text{TA}_0$  is the initial alkalinity (approximately 2.4 meq/l.). As both sulfate and bicarbonate are strongly complexed in sea water (GARRELS AND THOMPSON, 1962), one would expect that the relatively large changes in their composition, as encountered in pore waters of anoxic sediments, would have a marked effect on  $K_1'$ ,  $K_2'$  and  $K'_{\text{sp}}$ . This dependency was examined by estimating the values of the apparent constants, as a function of sulfate reduced, by the model of GARRELS AND THOMPSON (1962).

The mathematical procedure of these calculations is similar to the one described above, except that it was carried out as a function of alkalinity rather than total concentration of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ . The concentrations of these species were obtained through the constraint that the activity of bicarbonate and carbonate are related through the second dissociation constant of carbonic acid ( $K_2$ ). The value of  $\text{p}K_2$  was taken as 10.33 (BERNER, 1971).

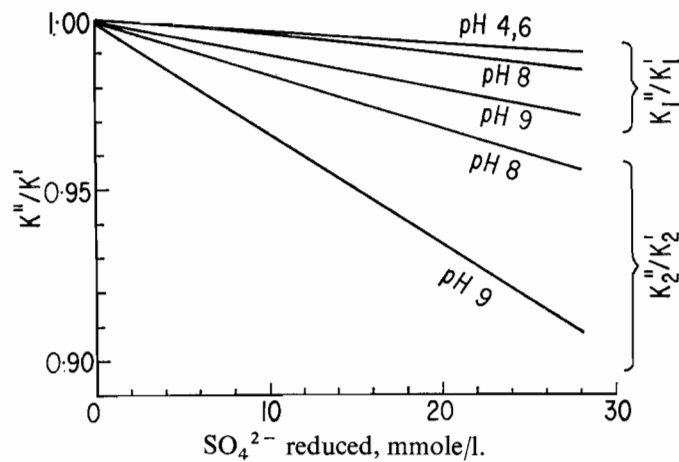


Fig. 1. Estimated variation of the first and second apparent dissociation constants of the carbonic acid in interstitial water of anoxic marine sediments as a function of sulfate reduced. The ordinate represents the ratio of calculated apparent dissociation constant for a given condition ( $K''$ ) to its calculated value in normal sea water ( $K'$ ).

The present model calculations (Figs. 1 and 2) demonstrate that the apparent constants of the carbonate system in sea water are pH dependent as a result of the pH dependence of carbonate-bicarbonate speciation (SKIRROW, 1965). The solubility of  $\text{CaCO}_3$  in interstitial water of anoxic marine sediments may increase by 2%, whereas  $K_2'$  may decrease by 5% relative to their value in normal sea water (Figs. 1 and 2). The expected change in  $K_1'$  is smaller, about -2%. The nomographs (Figs. 1 and 2) consider only the changes due to sulfate decrease and the resulting carbonate alkalinity increase. However, analyses of interstitial waters of marine sediment have shown (PRESLEY, 1969) that other changes, notably changes in calcium and magnesium con-

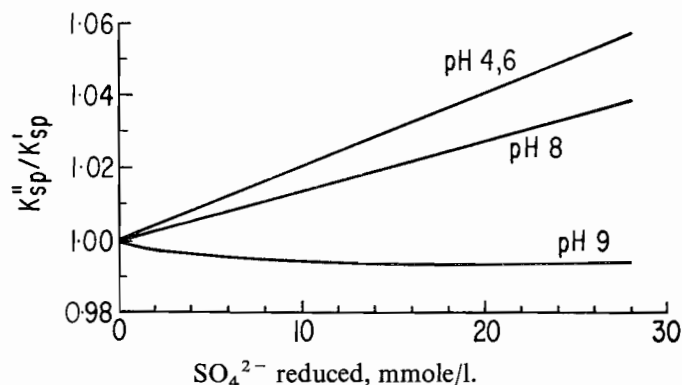


Fig. 2. Estimated variation of the apparent solubility product of  $\text{CaCO}_3$  in interstitial water of anoxic marine sediments as a function of sulfate reduced. The ordinate represents the ratio of calculated apparent solubility product of  $\text{CaCO}_3$  for a given condition ( $K''_{sp}$ ) to its calculated value in normal sea water ( $K'_{sp}$ ).

centrations, are also characteristic of these waters. Although no generalized conclusion regarding the variation of the apparent constant in interstitial waters can be made, the magnitude of the expected changes can perhaps be estimated by considering an extreme example. Table 2 reproduces results of SAYLES, MANHEIM and CHAN (1970) for core 27A of Leg IV of the Deep Sea Drilling Project (JOIDES) and the estimated changes of  $K'_1$ ,  $K'_2$  and  $K'_{sp}$  for each depth, as calculated from the model of GARRELS and THOMPSON (1962) and equations (4) and (6). These results suggest that the maximum variation of  $K'_1$  is 2%,  $K'_2$  is 7% and 11% for  $K'_{sp}$ .

#### SOLUBILITY OF $\text{CaCO}_3$ IN SEA WATER

EDMOND and GIESKES (1970) have recently reviewed the available experimental data related to  $\text{CaCO}_3$  solubility in sea water (WATTENBERG, 1933; WATTENBERG and TIMMERMANN, 1936; HINDMAN, 1943; MACINTYRE, 1965) and concluded that the solubility determination by MacIntyre for 19‰ Cl and 25°C is the most reliable. However, each investigator has used a different experimental procedure to determine  $\text{CaCO}_3$  solubility in sea water, and furthermore, in each case when equilibrium was finally established, the composition of the equilibrated solution was different from that of average sea water.

Consider, for example, the experimental procedure of MACINTYRE (1965). In most of his solubility experiments, he increased the partial pressure of  $\text{CO}_2$  of the tested solution to 1 atmosphere to enhance carbonate dissolution. However, calcium concentration in 1 atmosphere  $\text{pCO}_2$  waters saturated with respect to calcite was more than 100% larger than its concentration in sea water while the carbonate alkalinity increased by about ten-fold. In fact, examination of MacIntyre's raw data (some of these data are reproduced in Table 3) reveals that TA and calcium concentration in his test solutions were quite different from those of normal sea water.

As already pointed out, 'apparent constants' are constant only for a fixed ionic composition, and one may question, therefore, whether the apparent solubility constants determined by MACINTYRE (1965) are directly applicable to sea water. The compositional change, caused by the experimental procedure, may not only result in

Table 2. Estimated variation of the apparent constants of the carbonate system in interstitial waters of marine sediments. Calculations are for 19‰ Cl and 25°C

Hole	Depth below water (m)	Data of SAYLES, MANHEIM and CHAN (1970) recalculated to 19‰ Cl							Estimated changes in apparent constants			
		Na <sup>+</sup> (mmole/kg)	K <sup>+</sup> (mmole/kg)	Mg <sup>2+</sup> (mmole/kg)	Ca <sup>2+</sup> (mmole/kg)	SO <sub>4</sub> <sup>2-</sup> (mmole/kg)	TA (meq/kg)	K <sub>1</sub> ''/K <sub>1</sub> '	K <sub>2</sub> ''/K <sub>2</sub> '	K <sub>sp</sub> ''/K <sub>sp</sub> '		
27A	34	467	9.89	62.5	13.2	25.3	5.05	1.032	1.087	1.118		
	49	464	8.81	45.1	14.7	22.8	5.45	0.989	0.935	0.921		
	58	470	9.26	43.3	14.6	22.1	4.95	0.985	0.921	0.900		
27	147	472	5.87	42.2	20.6	17.2	2.76	1.007	0.948	0.925		
	239	458	5.32	40.4	24.3	10.9	4.24	1.015	0.951	0.923		
	246	434	5.43	38.8	25.4	10.1	3.31	1.011	0.937	0.901		
	374	437	4.80	32.0	28.4	4.51	1.39	1.007	0.896	0.837		

Table 3. Recalculated value of calcite  $K_{sp}$  and  $K'_{sp}$  from data of MACINTYRE (1965) for 19‰ Cl at 25°C.

Run No.	Original data from MACINTYRE (1965)				Recalculated		
	pH	TA (eq/l.) $\times 10^3$	Ca <sup>2+</sup> (mole/l.) $\times 10^2$	$K'_{sp}$ (mole <sup>2</sup> /l. <sup>2</sup> ) $\times 10^7$	$K_{sp}$ (mole <sup>2</sup> /l. <sup>2</sup> ) $\times 10^9$	$K'_{sp}$ (mole <sup>2</sup> /l. <sup>2</sup> ) $\times 10^7$	
15	6.23	20.66	1.94	5.4	3.49	5.04	
16	6.04	26.09	2.20	5.1	3.18	4.59	
17	6.25	21.90	2.07	6.2	4.13	5.97	
18	6.22	20.75	1.94	5.3	3.45	4.98	
19	6.21	22.42	2.03	5.9	3.75	5.41	
20	6.26	20.28	1.92	5.5	3.64	5.26	
21	6.22	21.99	2.00	5.8	3.75	5.41	
22	8.38	2.84	0.132	5.0	3.34	5.36	
23	6.09	24.85	2.15	5.1	3.34	4.82	
24	6.14	23.87	2.10	5.5	3.51	5.07	
25	6.16	23.77	2.09	5.7	3.66	5.28	
26	6.15	23.82	2.10	5.7	3.58	5.17	
27	6.15	23.71	2.09	5.6	3.55	5.12	
28	6.15	24.18	2.12	5.7	3.66	5.29	
29	6.4	24.28	2.12	5.6	3.60	5.20	
Average:					5.54	3.58	5.20

a change in  $K'_{sp}$ , but also in  $K_1'$  and  $K_2'$ . The change in the latter is of particular importance, because  $K_2'$  was used to calculate  $K'_{sp}$  from the raw experimental data. The value of total concentration of  $\text{CO}_3^{2-}$ , required to determine  $K'_{sp}$  was estimated by MACINTYRE (1965) from alkalinity and pH data through the relation (SKIRROW, 1965):

$$[\text{CO}_3^{2-}]_t = \text{CA} \frac{K_2'}{a\text{H} + K_2'} \quad (12)$$

However, because  $K_2'$  by itself is also a function of alkalinity and calcium concentration, MacIntyre may have been in error when using the value of  $K_2'$  assigned to sea water (LYMAN, 1957).

The model of GARRELS and THOMPSON (1962) in conjunction with equations (4) (6) enables one to estimate the variation of  $K_1'$ ,  $K_2'$  and  $K'_{sp}$  as a function of calcium concentration and carbonate alkalinity. The remaining ions were assumed to be in the concentration of sea water of 19‰ Cl at 25°C. The normalized results of these calculations are given in Figs. 3, 4 and 5. It is evident from these figures that neither  $K_2'$  nor  $K'_{sp}$  can be considered to be constant over the range of the compositional changes encountered in the carbonate solubility experiments of MacIntyre. For example, the apparent solubility constant ( $K''_{sp}$ ) in 'sea water' in which the calcium concentration is twice that of average sea water and the carbonate alkalinity is 20 meq/l. at pH 6 (typical of MacIntyre's experiment), is approximately 9% larger than that of the solubility of the same mineral in normal sea water (Figs. 3 and 4). However,  $K_2'$  which was used to determine  $K'_{sp}$ , is about 2% too large (Figs. 4 and 5), and as a result of these two opposing effects, the apparent solubility product reported by MacIntyre is about 7% greater than the correct value.



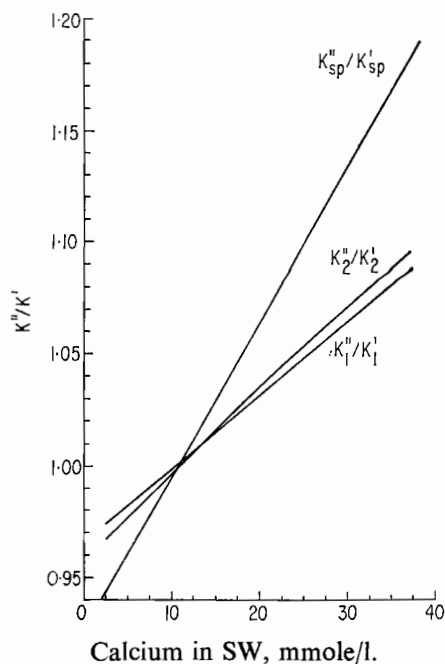


Fig. 3. Estimated variation of the apparent constants of the carbonate system in modified sea water as a function of calcium concentration. Estimations are for 19‰ at 25°C.

The apparent solubility product for sea water ( $K'_{sp}$ ) was obtained from MacIntyre's data by first re-calculating  $K''_{sp}$  for the given experimental conditions (taking into account the variation in  $K_2'$ ), and then dividing it by  $K''_{sp}/K'_{sp}$  calculated for each case. The average recalculated solubility (Table 3) is  $5.20 \times 10^{-7}$  mole<sup>2</sup>/l.<sup>2</sup>, which is lower by about 6.3% than the value reported by MacIntyre and accepted by EDMOND and GIESKES (1970). The difference is larger than the uncertainty range ( $\pm 5\%$ ) assigned by Edmond and Gieskes to MacIntyre's solubility values. Table 3 also gives the thermodynamic solubility product calculated from MACINTYRE'S (1965) raw data by the model of GARRELS and THOMPSON (1962). The average value is

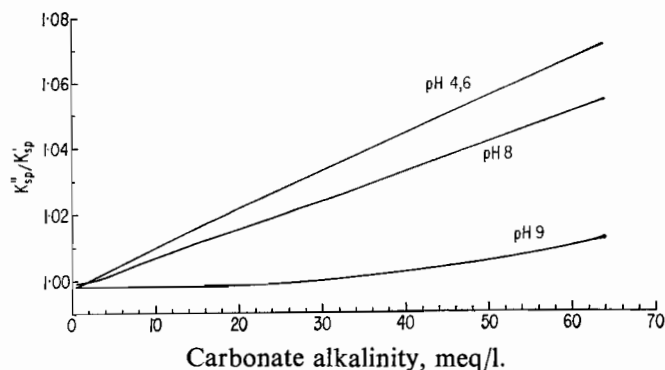


Fig. 4. Variation of the apparent solubility product of  $\text{CaCO}_3$  in modified sea water as a function of carbonate alkalinity.

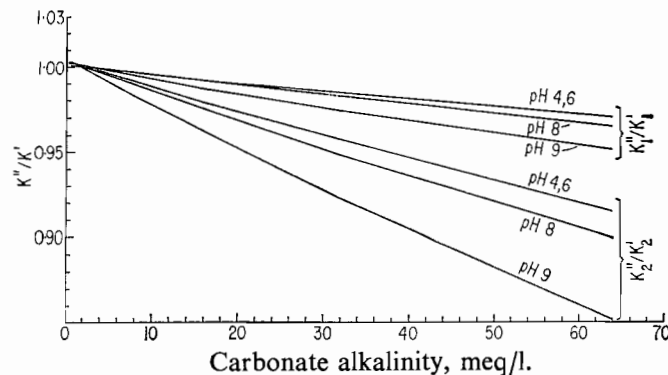


Fig. 5. Estimated variation of the apparent dissociation constants of carbonic acid in modified sea water as a function of alkalinity.

$3.58 \times 10^{-9}$  mole<sup>2</sup>/l.<sup>2</sup> as compared to  $4 \times 10^{-9}$  suggested by LANGMUIR (1968). The 0% difference is well within the accuracy of the model of Garrels and Thompson (THOMPSON and ROSS, 1966; BERNER, 1971).

It is interesting to note that the re-calculated values of  $K'_{sp}$  from the data of WATTENBERG and TIMMERMANN (1936) are larger by about 5% than the original values given by them (as re-calculated by EDMOND and GIESKES to 19‰ at 25°C). This reduces the difference between the values of  $K'_{sp}$  recalculated from MacIntyre's data and those recalculated from the data of Wattenberg and Timmermann from about 30% to approximately 20%.

EDMOND and GIESKES (1970) observed that the solubility data of WATTENBERG and TIMMERMANN (1936) are pH-dependent and concluded that this phenomenon indicates an experimental error which they attributed to the quinhydrone electrode used by Wattenberg and Timmermann. However, examination of Fig. 4 reveals that solubility of  $\text{CaCO}_3$  in modified sea water is indeed pH-dependent. This dependence is particularly important at low pH values and at high carbonate alkalinities. This general behavior is clearly detected upon close examination of the experimental data of Wattenberg and Timmermann. It is therefore probable that the pH-dependence of the reported  $K'_{sp}$  data is not entirely due to malfunction of the quinhydrone electrode, as suggested by Edmond and Gieskes, but also reflects the pH-dependence of  $\text{CaCO}_3$  solubility in sea water of high alkalinity.

#### DISCUSSION AND CONCLUSIONS

The present numerical analyses support the observation already made by many workers in the past that the 'apparent constants' are not independent constants, but are a function of the ionic environment. It appears (Table 1) that for open waters these parameters can be considered constants—to within the uncertainty in their values (EDMOND and GIESKES, 1970). Application of these 'constants' to modified sea water, either natural or artificial, may result in an error. The exact magnitude of these errors cannot be accurately estimated due to the uncertainties in the model of Garrels and Thompson (THOMPSON and ROSS, 1966; BERNER, 1971). However, the present study suggests that the limits of variation of the apparent constants in the marine realm is in the order of  $\pm 10\%$ .

THOMPSON and ROSS (1966) reported that direct measurements of calcium activity in sea water suggest that about 84% of the calcium is free as compared to the figure of 91% suggested by the model of GARRELS and THOMPSON (1962), which was applied here. If this estimate is correct, then the sensitivity of carbonate solubility to calcium concentration is probably larger than calculated here. This would also imply that the values of calcite solubility in sea water of 19‰ Cl at 25°C reported by MacIntyre are too high by more than 6.3%.

MILLERO and BERNER (1972) have recently examined the measured pressure effect, and the estimated pressure effect, of  $\text{CaCO}_3$  solubility in sea water. They showed that the pressure effect estimated from partial molal volume data using the ion-pairing model of MILLERO (1969) is larger than the pressure effect measured by PYTKOWICZ and FOWLER (1967) and HAWLEY and PYTKOWICZ (1969) as reviewed by EDMOND and GIESKES (1970). It was concluded, therefore, that a larger portion of the ocean is undersaturated with respect to  $\text{CaCO}_3$ , compared to estimates of PYTKOWICZ and FOWLER (1967) and HAWLEY and PYTKOWICZ (1969). However, if our analysis is accepted, then the uncertainty in MACINTYRE's (1965) data (which was used to estimate the degree of  $\text{CaCO}_3$  saturation in the Pacific) partially compensates the correction suggested by MILLERO and BERNER (1972). In fact, the results of the *in situ* measurements of BEN-YAAKOV and KAPLAN (1971) suggest that the Pacific is less undersaturated than estimated by HAWLEY and PYTKOWICZ (1969).

The uncertainty in  $K_1'$ ,  $K_2'$  (EDMOND and GIESKES, 1970) and  $K'_{sp}$  seems to be particularly large when compared to the reported accuracies of recently-developed experimental techniques used to study the carbonate system in the ocean: 0.17% for alkalinity (EDMOND, 1970); 0.2% for total dissolved inorganic  $\text{CO}_2$  (WONG, 1970); 1% for  $\text{pCO}_2$  (BROECKER and TAKAHASHI, 1966); and 0.006 pH units for pH (PYTKOWICZ, KESTER and BURHENER, 1966). It appears that the precision and accuracy of the experimental techniques have surpassed the accuracy assigned to the apparent constants. Until the apparent constants are re-determined with higher accuracy, it is probably preferable to directly measure a given carbonate parameter than to calculate it from another quantity by using the apparent constants.

The results of the present study can be used to assess the errors that may be introduced when the apparent constants are determined in modified sea water. It appears that  $K_2'$  and  $K'_{sp}$  are sensitive to variation in sea water composition and it is therefore recommended that their re-determination be made in sea water of normal composition.

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